Network Growth in the Flocculation of Concentrated Colloidal Silica Dispersions

The physical basis behind the flocculation of colloidal liquids to gels is intricately related to the formation of clusters through adhesive contacts followed by network connectivity. In the experiments reported here on concentrated colloidal silica dispersions, small-amplitude dynamic shear rheology is used to measure macroscopic mechanical properties, and time-resolved small-angle x-ray scattering is used to obtain information regarding local structural ordering. These experiments suggest a picture in which the majority of adhesive contacts are established early in the process, within the "induction period," but the resulting clusters are only tenuously connected. The study has given some simple insight into an otherwise complex physical problem involving numerous dynamic and structural constraints.

Flocculation of a colloidal liquid to form a solid, elastic gel is a common yet dramatic transformation. It is exploited in manufacturing such diverse products as cheese, cosmetics, and ceramics, but creates practical problems in formulating colloidal dispersions. Flocculation occurs when long-range repulsive forces, such as electrostatic repulsion between like-charged colloids, are insufficient to prevent the association of pairs of particles, which are then subsequently held together by strong, short-range atomic adhesive forces. A charge-stabilized colloidal dispersion can be flocculated by the addition of electrolyte ions, which screen the surface charges on the particles. Multiparticle clusters are built up by successive coupling events and, at sufficiently high concentrations, a network of adhesive contacts may ultimately extend over the entire sample. The resulting gel exhibits solid-like mechanical properties governed by the volume fraction, connectivity, and strength of the network. Many, though not all, flocculated gels exhibit complex behaviors, such as thixotropy and syneresis. Thixotropy describes the "ketchup effect," whereby liquid-like flow can be shortly restored by subjecting a gel to a stress of sufficient magnitude to disrupt the structure, after which the initial properties gradually recover with time. Syneresis refers to the spontaneous shrinkage of a gel as it exudes excess solvent.

Extensive research on flocculation has yielded fundamental insights and useful generalizations regarding the pair potentials [1], kinetics of dimerization [2], and growth of extended clusters in dilute dispersions [3]. By contrast, our understanding of flocculated gels is still very primitive due to both theoretical and experimental limitations. Physical models describing the early stages of flocculation do not include multiparticle interactions that play a significant role at concentrations typical of flocculated gels (e.g., >10% by volume). Experimental characterization of gels is greatly complicated by the wide range of relevant times and dimensions involved and by the limited number of tools available to study highly concentrated systems.

To gain a better understanding of these issues, we investigated the growth of a flocculated network in a pure, well-characterized colloidal dispersion [4]. Parallel measurements were made under identical conditions on the evolution of local structure in the immediate neighborhood of each particle, and on the evolution of macroscopic mechanical properties. Small-angle x-ray scattering (SAXS) measurements, performed at the DND-CAT at the Advanced Photon

Source (APS), provided the structural information, while mechanical properties were measured via small-amplitude dynamic shear rheology. The time-resolved SAXS measurements were made possible by the high brightness available at the APS, since only a few seconds of data acquisition were required to obtain high-quality data over the appropriate scattering lengths. The rheometry measurements provided information on both the storage modulus G′ and the loss modulus G″ (corresponding to the elastic and viscous resistance to shear, respectively).

Our experiments employed very pure colloidal silica particles, 870 ± 40 Å in diameter, as shown in the electron micrograph in Fig. 1. These particles are negatively charged and were initially prepared as stable liquid dispersions up to 53.7% by weight in deionized water. Flocculation was initiated by rapidly mixing with concentrated aliquots of $MgCl_2$. Even after more than a year, no evidence of syneresis was observed in this system.

Figure 2 shows the growth in the storage modulus G′ with time, following both the initial *de novo* addition of $MgCl_2$ and the subsequent application of a large-amplitude shear to disrupt the network after several hours of growth. The curve labeled *de novo*, measured under very low deformation conditions, shows the storage modulus as a function of time after mixing the particles with a $MgCl_2$ solution.

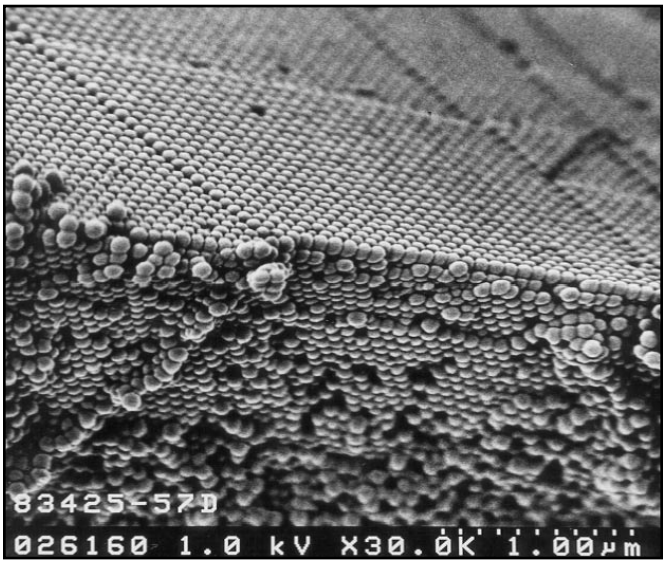

FIG. 1. Scanning electron micrograph of dried stock dispersion sample, with no salt. Scale bar is 1.0 µm.

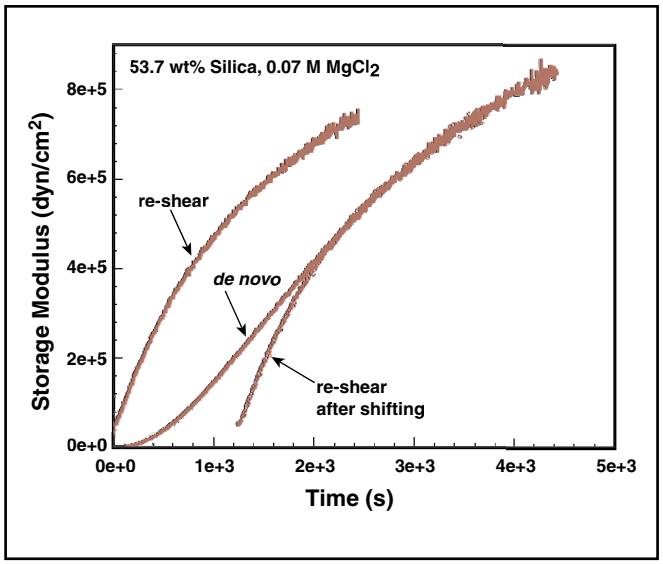

FIG. 2. Storage modulus of a 53.7 wt % SiO_2 sample in the presence of 0.07 M $MgCl_2$ as a function of time after mixing the particles with $MgCl_2$ solution (curve labeled de novo*), and as a function of time after vigorously shearing the resultant gelled sample (curve labeled re-shear). The data points (labelled as rear-shear after shifting) are the result of shifting the re-shear data by 1240 s along the time axis to allow overlap with the long-time regime of the* de novo *data.*

After an initially slow "induction" period lasting approximately 1300 s, the stiffness increases rapidly, eventually saturating above 10^6 dyn/cm^2. This increase arises from changes in the particle aggregation and/or connectivity of the aggregated network. Subsequently, the sample was subjected to very high shear rates, and then the measurement was repeated. The curve labeled "re-shear" shows that this is indeed a thixotropic material: the storage modulus returns to a very low value after vigorous shearing. However, the sample does not return to its original state after re-shear, but starts over with a significantly higher elastic modulus. The effect is the same as if the "induction" period had just been skipped, and indeed the "after shifting" curve shows that the structural evolution of the re-sheared sample eventually becomes the same as that of the *de novo* sample. This strongly suggests that upon re-shearing, the sample is not broken down into individual particles, but rather into clusters of particles that then reassemble upon cessation of shear.

The SAXS measurements highlight a very different part of the story. As seen in Fig. 3(a), the scat-

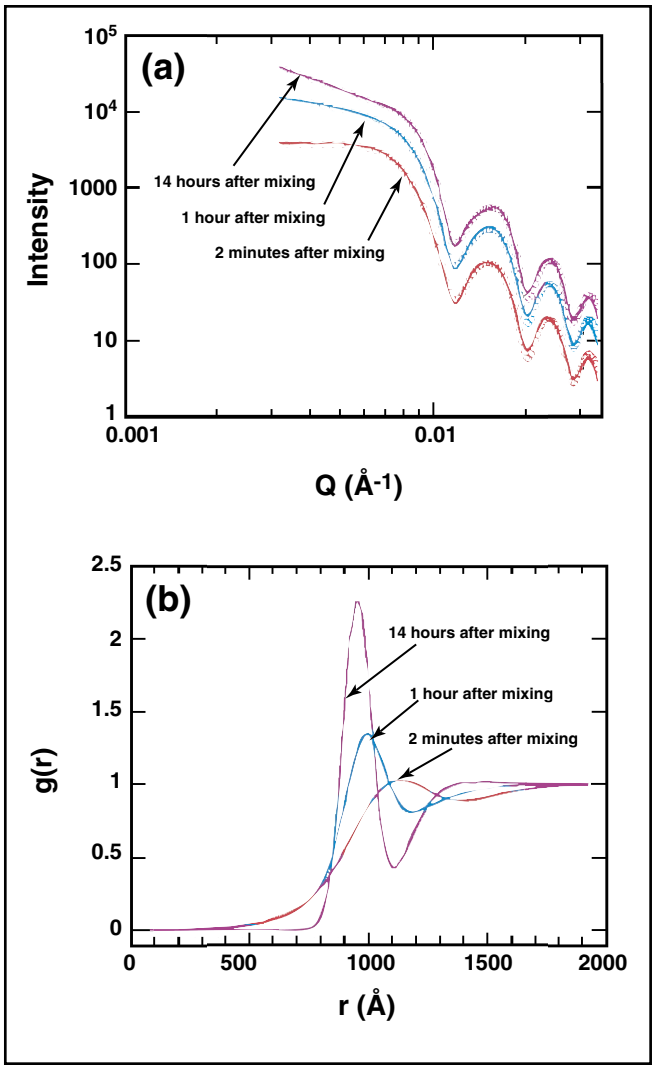

FIG. 3. (a) SAXS intensity and model for a 31.7 wt% SiO_2 sample in the presence of 0.050 M $MgCl_2$ at indicated times after mixing. For clarity, scans are offset along the intensity axis. (b) The real space radial distribution functions used in analyzing the data shown in (a).

tered intensity measured as a function of the momentum transfer $q = (4\pi/\lambda) \sin\theta$ shows an oscillatory pattern due to the spherical shape of the silica particles, which is modified at low q by the short-range interparticle correlations. These correlations are characterized by the radial distribution function $g(r)$, which describes the relative probability of finding two particles whose centers are separated by distance r, normalized so that $g = 1$ is just the random probability of finding a particle at any distance. The limiting value of $g(r)$ at large distances is 1, while at distances shorter than a particle diameter, $g(r) = 0$, because of the impossibility of superimposing particles. Figure 3(b) shows the approximations of $g(r)$ that were found to be in best agreement with the SAXS data. During the initial induction period, the environment of each particle becomes better ordered, with an increase in the probability of contact at a distance of exactly one particle diameter (870 Å). A corresponding decrease in $g(r)$ near $r = 1000$ Å indicates that the number of contacting neighbors grows at the expense of neighbors slightly farther removed. Surprisingly, after the first few hours, virtually no further changes in local structure could be detected despite the dramatic increase in G′ over much longer times. Furthermore, no changes were observed in the SAXS pattern when the sample was re-sheared.

Taken together, these experiments suggest a picture in which the majority of adhesive contacts are established early in the process, within the "induction period" exhibited in G′, but the resulting clusters are only tenuously connected. Over longer times, extremely small increases in the number of contacts per particle are apparently sufficient to greatly increase G′. This is perhaps not surprising when one considers that only one new contact is required to join two arbitrarily large clusters. It is tempting to imagine that the same physical constraints responsible for conserving the total number of neighbors within the first few particle diameters are also responsible for the conservation of gel volume (the absence of syneresis) and for ultimately limiting the extent of coupling and growth in G′, but the identity of those constraints remains to be determined.

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References

[1] E.J.W. Verwey and J.Th. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).

[2] R. Buscall, I.J. McGowan, P.D.A. Mills, R.F. Stewart, D. Sutton, L.R. White, and G.E. Yates, J. Non-Newt. Fluid Mech. **24**, 183 (1987).

[3] M.Y. Lin, H.M. Lindsay, D.A. Weitz, R. Klein, R.C. Ball, and P. Meakin, Proc. Royal Soc. A **71**, 423 (1989) and references therein.

[4] P.A. Heiney, R.J. Butera, J.D. Londono, R.V. Davidson, and S. Mazur, J. Phys. Chem. B **104**, 8807 (2000).

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